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KINETIC CONSTANTS OF DECOMPOSITION OF THE MUNICIPAL
SOLID WASTE PRIOR TO AND AFTER
MECHANICAL-BIOLOGICAL PROCESSING.
FIELD SCALE

MONIKA SUCHOWSKA-KISIELEWICZ*, ANDRZEJ JĘDRZAK,
SYLWIA MYSZOGRAJ

University of Zielona Gora
The Institute of Environmental Engineering
Licealna 9, 65-417 Zielona Gora, Poland

*Corresponding author's e-mail: M.Suchowska-Kisielewicz@iis.uz.zgora.pl

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Abstract: One of the major tasks of municipal waste management in European Union countries is the systematic reduction of waste that is removed and transported to landfills. This refers particularly to biodegradable waste. One of the methods employed to decrease waste amount is Mechanical-Biological Treatment (MBT) of the waste, before it is stored.

The article presents characteristics of MSW and biologically pre-treated municipal solid waste, organic carbon loads emitted in biogas and leachate during waste deposition in a landfill. Its decomposition rate constants were determined on the basis of modified Zacharof and Butler's stochastic model. The values of decomposition rate constants determined for MSW had similar change trends to those presented in the literature: the hydrolysis constant had the lowest value ($2.6 \times 10^{-5} \text{ d}^{-1}$), the highest acid phase constant ($4.1 \times 10^{-4} \text{ d}^{-1}$), while the methane phase constant – $2.2 \times 10^{-4} \text{ d}^{-1}$. The PMSW decomposition rate constants in each anaerobic waste degradation phase had similar change trends, though their values were higher, by 21, 11 and 19%, respectively.

INTRODUCTION

Waste decomposition processes

One of the major tasks of municipal waste management in European Union countries is the systematic reduction of waste that is removed and transported to landfills. This refers particularly to biodegradable waste [27]. The presence of such waste influences the amount of pollution emitted with leachate and biogas to the natural environment. Poland adopted The Directive on the Landfill of Wastes 1999/31/EEC requiring the reduction of biodegradable waste by 25% to 2010, by 50% to 2013 and 65% by 2020, in relation to the amount of landfill waste in 1995 [4]. One of the methods employed to decrease waste

amount is Mechanical – Biological Treatment (MBT) of the waste, before it is stored. The method has been recommended in The Polish National Waste Management Plan 2010 as useful for regions of population between 150,000 and 300,000 people. MBT allows for reducing the organic pollution and nitrogen emissions, present in leachate and biogas, by even 80–90% [2, 19, 22]. The emission reduction scale depends on a number of factors: the waste composition (the percentage of organic biodegradable substance), a type of utilized method, the conditions of biological stabilization process and duration of the degradation [21].

Biological processes taking place at the landfill may be basically divided into three phases. Each phase has its specific requirements and each generates specific products. Each phase is distinguished on the basis of the physical-chemical composition of leachate, as well as the quantity and quality of biogas production [20]. According to various scientific sources, the waste decomposition process may have three [14], four [20, 26] or five phases [17, 18]. For practical reasons, the most frequently applied is divided into three phases, consisting of hydrolysis, acid phase and methane phase. The first phase includes disintegration, waste dissolution and enzymatic reactions of the hydrolysis. The final products of hydrolysis (monosaccharides, aminoacids, long-chain organic acids and glycerol) become a substrate for the acid phase, during which they are transformed by bacteria into short-chain organic acids (formic, acetic, propionic, butanoic, valeric and hexanoic acids), alcohols (methanol, ethanol), aldehydes and gases (carbon dioxide, hydrogen). They in turn become a substrate for acetate and methanol bacteria. Hence, the efficiency of decomposition process depends on the rate of hydrolysis and the balance between the substrate production during acid and methane phases. A detailed analysis and modeling of hydrolysis mechanisms as well as acid and methane phases enables one to elaborate adequate methods oriented at intensification of decomposition processes and prediction of pollution emission period at landfills [26].

Waste decomposition models

The anaerobic waste decomposition kinetics is described by numerous mathematical models. Most of them employ the assumption that in a wide range of conditions present during the anaerobic decomposition processes, the hydrolysis is the slowest, thus it determines the rate of decomposition in general.

According to Bastone *et al.* [1] hydrolysis may be described by two basic models that reflect two different concepts.

The first one is the Michaelis-Menten kinetic model (1) which assumes the rate of hydrolysis by the rate of microorganisms' growth:

$$\frac{dS}{dt} = k \cdot E \frac{S}{K_m + S} = V_m \frac{S}{K_m + S} \quad (1)$$

where: S, E – the concentration of substrates and enzymes, k – hydrolysis rate constant, V_m – maximum hydrolysis rate, K_m – half-saturation rate coefficient.

Another model, widely applied and presented in the literature, utilizes the first order equation to describe the hydrolysis process (2). According to this model, the

hydrolysis rate depends on the presence of organic substrates, which are easily available to microorganisms:

$$\frac{dS}{dt} = -kS \quad (2)$$

where: S – substrate concentration, k – the first-order rate coefficient.

More developed models employ much more complicated formulas to describe processes of waste decomposition and to predict the amount of pollution to be removed with leachate and biogas. These formulas allow for calculating the rate of decomposition in each phase: hydrolysis, acid and methane phase. As a consequence, it leads to more accurate reflection of the process [5, 6, 30]. In the aforementioned models, the changes in amount of organic carbon are determined in three phases: solid phase (waste), liquid (leachate) and gas (biogas). Such an approach is represented by the El-Fadel *et al.* [5, 6] model as well as the Zacharof and Butler's [30] model.

El-Fadel *et al.* [5, 6] utilizes Monod's equation to describe the kinetics of fermentation, considering the rate of growth and decay of microorganisms in each decomposition phase. This model requires a lot of data describing the variation of waste composition and process conduction conditions, which are difficult to determine [6, 11, 28, 29]. Therefore this model has a high uncertainty level. The Zacharof and Butler's [30] model uses stochastic equations that take into account – like El Fadel *et al.* [5, 6] model – the influence of the growth rate and concentration of microorganisms upon the decomposition process. Unlike the El Fadel *et al.* [5, 6] model, however, in the case of Zacharof and Butler's model it is not necessary to identify so many uncertain parameters that describe the process.

Zacharof and Butler's [30] model describes the process of hydrolysis using the first order reaction, whereas the growth and decay of microorganisms during the following phases are presented by means of the below equation (3):

$$R(t) = Ate^{(-kt)} \quad (3)$$

where: $R(t)$ – reaction rate at time t , kg/year; A – amplitude term, kg/year²; k – rate constant, year⁻¹.

The value of $R(t)$ function (Fig. 1) in the model depends on the rate of microorganisms' growth.

The function itself describes two phases of the process. The first stage, during which the function $R(t)$ value rises rapidly, is a period of fast exponential growth of microorganisms due to the high availability of readily degradable organic substrates (dissolved organic carbon). The second stage, during which there is a characteristic and clear decline of values exponentially approaching zero, displays a moderation of microorganisms' growth due to a depletion of dissolved organic carbon.

The changes of the organic carbon content in waste are described by the following formulas (4) – (7) in the Zacharof and Butler's [30] model:

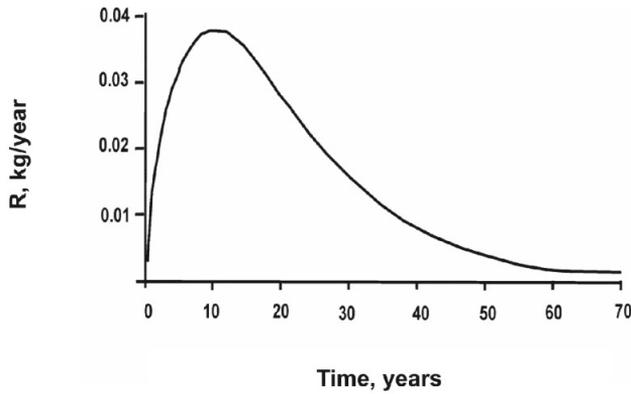


Fig. 1. The growth and decomposition function $A=0.01$ kg/year², $k=0.1$ year⁻¹ [30]

The changes of carbon mass in solid waste during hydrolysis – solid phase

$$\frac{dm_{i(s)}}{dt} = -k_h m_{i(s)} \quad (4)$$

the changes of dissolved carbon mass – liquid phase

$$\frac{dm_{i(Aq)}}{dt} = k_h m_{i(s)} - A_a t e^{(-k_a t)} \quad (5)$$

the changes of carbon mass in acetate phase – gas phase

$$\frac{dm_{i(Ac)}}{dt} = A_a t e^{(-k_a t)} - A_m t e^{(-k_m t)} \quad (6)$$

the changes of carbon mass in methane phase – gas phase

$$\frac{dm_{i(Me)}}{dt} = A_m t e^{(-k_m t)} \quad (7)$$

where, m_i – ‘i’ – mass of this component.

The following symbols S , Aq , Ac and Me denote correspondingly: solid mass, dissolved mass, acetate mass and methane mass. Indices h , a and m denote the rate constants for hydrolysis, acid phase and methane phase. A_a and A_m symbols describe the amplitudes of acetate and methane decomposition.

Waste decomposition rates

The literature contains a lot of information about the decomposition rate of municipal solid waste (MSW) [7–10, 12, 15, 24, 25] but there is a scarcity of information about the

decomposition rate of pre-treatment municipal solid waste (PMSW). The research results reveal that the decomposition rate of MSW is tightly correlated with its composition. The first order hydrolysis takes values from 10^{-7} d^{-1} for slow – degradable fraction [7] to 0.55 d^{-1} for food leftovers [25]. Low rate constant values are typical for ingredients with high contents of lignin and cellulose, such as scrap paper or straw. Vavilin *et al.* [26] provided the following first order constant values for cellulose (0.066 d^{-1}), office paper (0.036 d^{-1}), cardboard (0.046 d^{-1}) and newsprint (0.057 d^{-1}). The value for MSW is 0.1 d^{-1} . Garcia de Cortazar and Monzon [7] give the first order hydrolysis value of $2.3 \cdot 10^{-4} \text{ d}^{-1}$ for the readily biodegradable MSW fraction, and rate constant values for acid and methane phases – 0.01 and 0.02 d^{-1} respectively. For the slow biodegradable fractions, the rate constant values were 10^{-7} , 10^{-4} and 10^{-5} d^{-1} respectively. Manna *et al.* [13] determined the hydrolysis first order constant value of organic waste at $1.89 \cdot 10^{-3} \text{ d}^{-1}$. Musmeci [15] adopted the hydrolysis rate constant values of composted waste (various mixtures of grass, leaves and cardboard) from 0.165 to 0.190 d^{-1} .

Komilis *et al.* [10] presented the hydrolysis rate constants of rapidly biodegradable fraction (k_{hr}) and moderately biodegradable fraction (k_{hr}) respectively of paper waste (0.06, 0.005 d^{-1}), vegetable waste (0.09, 0.008), food leftovers (0.1, 0.05), as well as tree branches (-, 0.06), leaves (-, 0.03) and grass (-, 0.03), subjected to separate composting in laboratory conditions.

A considerable diversification of constant values presented in the literature is a result of examining the waste of different composition and fragmentation, stabilized in different technical and technological conditions, having different hydrolytic biomass to substrate ratio.

The article presents the characteristics of MSW and PMSW (stabilized in aerobic conditions for about 5 weeks) and organic carbon loads emitted in biogas and leachate during storing of these wastes on a landfill. Modification of stochastic Zacharof and Butler's [30] model was proposed, which involved the introduction of a stochastic random disturbance component considering the influence of variable waste storage conditions, being difficult to describe, on the process. Based on the modified model, the decomposition rate constants were determined in each degradation phase (the hydrolysis, the acid and the methane phases) of MSW and PMSW at the landfill.

MATERIAL AND METHODS

Research material

Research was carried out on municipal solid waste (MSW, unprocessed biologically) and pre-treated waste (PMSW), collected from central heated block of flats in Zielona Gora. Biological processing was conducted in Municipal Waste Composting Plant in Zielona Gora. The biological line installation consisted of four oxygen open chambers made of reinforced concrete. Every 7–10 days the waste was moved to another chamber. The overall waste stabilization time was approximately five weeks. The waste was aerated by sucking out gasses from the bottom of the chambers.

MSW samples weighing 50 kg were taken from randomly selected vehicles which deliver waste from tall buildings of the city of Zielona Gora to the bunkers, and waste samples of PMSW from selected batches of composted waste. Each of the MSW and PMSW samples was exposed towards screening of the following granulometric

fractions: <10 mm, 10–20 mm and >20 mm. The 10–20 mm fraction was manually sorted to the fraction of biodegradable waste (kitchen, garden, wood, paper and card board, textiles made from natural fibers, composite waste and skin), and non-biodegradable waste. The fraction < 10 mm was added to the biodegradable fraction in the proper proportion. The fraction >20 mm was divided in to successive granulometric fractions: 20–40 mm, 40–60 mm, 60–100 mm and >100 mm in order to simplify sorting it to material. The separated material fractions (>20 mm) were manually or mechanically crushed to grains of grain size below 10 mm. All separated granulometric and material fractions were weighed and their weight in the overall mass of waste was determined. The fraction <10 mm and biodegradable and non-biodegradable fraction 10–20 mm and the material fraction (>20 mm), after mechanical or manual crushing to the grain of grain size below 10 mm were reduced by quartering to obtain a sample weighing about 0.5 kg. Physicochemical composition in the prepared samples was tested.

The research area

The examined waste was placed in two reinforced concrete bunkers, which are part of the composting plant technological line. Each bunker has the following dimensions: (Length × Breadth × Height) and active volume $L \times B \times H = 44.30 \times 4.72 \times 3.10$ m. The waste was placed in layers of 20–25 cm thickness, and compressed by a light bulldozer. As a result, the MSW layer thickness measured 0.69 Mg/m^3 , and PMSW thickness was 0.56 Mg/m^3 .

The bunkers were equipped with leachate and biogas intake systems. The leachate was drained with a drainage pipeline, placed on each bunker's bottom and equipped with a water-meter. The outlet and leachate sample collecting point were located in a ventilation room. The leachate reception system consists of flow tank (volume – 5 dm^3), where samples were taken, and the end tank (volume – 50 dm^3). When the collected leachate exceeded a limiting level in the end tank, it was pumped into the composting plant sewerage system. The leachate draining pipelines were equipped with air traps so as to prevent the air being sucked into the leachate deposit.

Biogas collecting drainage pipelines were installed along bunkers at two levels – 0.5 m above the bunker bed and 1 m below the waste surface. Biogas collecting spouts were put out, along side walls of the bunkers.

Testing procedure

After bringing the waste into the bunker, the amount of leachate forming was monitored on a daily basis. A daily amount of leachate was assessed upon the indications on the water – meter.

The leachate samples for physical-chemical composition examination were initially collected twice a week (between the 1st and 122nd day of research), then once a week (between 123rd and 365th day) and finally, during the last stage of testing – once in three weeks (between 366th and 915th day). Twenty-four hours before each sample collection, the sample collection tank had been emptied. Biogas was sucked in from the bottom pipeline (placed 0.5 m over the bottom) with a Metrix G 2.5 type gas-meter operating within the capacity range between 600 and $20 \text{ dm}^3/\text{h}$, till the gas pressure in the top pipe was balanced out. During the first year of testing, the biogas was measured twice a week, and in the second and the third years, once a week. The biogas was measured in

equal time intervals once in 15 minutes. With the measuring instrument, the amount and composition of biogas was established.

Process control

The process control included the analyses of sieve, chemical and composition of the waste, the leachate quantity measurement and its chemical composition, biogas chemical composition and the monitoring of rainfall.

The waste and leachate analyses were conducted according to Polish valid norms. The quantity of leachate was assessed upon daily readouts from water-meter installed on the leachate drain pipe.

Daily and total precipitation quantities were determined upon monthly reports obtained from a nearby weather station.

Modified equations of Zacharof and Butler's model

The Zacharof and Butler's model has been employed for the purpose of modeling the processes taking place at the landfill. In order to give consideration to all factors that influence decomposition processes (temperature, pH, moisture content, composition of waste), equations of the aforementioned model needed to be modified. The modification included incorporating a stochastic factor of the form random disturbances (8) to the right sides of equations (4) and (5):

$$\gamma(t)m_{i(s)}B_t \quad (8)$$

where: $\gamma(t)$ – the function determining the influence intensity of randomly occurring disturbances; $(B(t))_{t \geq 0}$ – the function describing all disturbances that influence the course of a process (so called 'white noise').

Incorporating the term (8) to equations (9) and (10) allows for taking into account unpredictable and difficult to assess factors influencing the process. The reason for their unpredictability is the complexity of occurrences taking place at the landfill, as well as the heterogenic character of the waste. The elements were incorporated as random factors that constitute a probability space (Ω, F, P) , where: F stands for the family of all subsets of the Ω ensemble that contains all the random factors disturbing processes taking place at the landfill. The C stands for occurrence probability of distinguished group of factors $A \in F$ during the observed process.

Ultimately, the following equations were elaborated:

carbon mass changes in solid waste – hydrolysis

$$dm_{i(s)}(t) = -k_h(t)m_{i(s)}(t)dt + \gamma(t)m_{i(s)}(t)dB_t \quad (9)$$

dissolved carbon mass change – liquid phase

$$dm_{i(Aq)}(t) = (k_h(t)m_{i(s)}(t) - A_a(t)te^{-ka(t)})dt - \gamma(t)m_{i(s)}(t)dB_t \quad (10)$$

carbon mass changes during acetate phase – gas phase

$$dm_{i(Ac)}(t) = (A_a(t)te^{-tka(t)} - A_m(t)te^{-tkm(t)})dt \tag{11}$$

carbon mass changes during methane phase – gas phase

$$dm_{i(Me)}(t) = A_m(t)te^{-tkm(t)}dt \tag{12}$$

where: A_a , A_m , k_h , k_a and k_m , are the functional parameters describing the rates of biochemical transformations proceeding in the landfill (the symbol „h” stands for the hydrolysis process, the symbol „a” stands for the acid phase processes, and the symbol „m” denotes the methane phase processes).

The basic problem connected with determining the above-mentioned masses based on the measurements of their values at the points of time $0 < t_1 < t_2 < \dots < t_r = T$, is the determination of the functions A_a , A_m , k_h , k_a and k_m . It requires the appropriate setting of the numbers A_a^j , A_m^j , k_h^j , k_a^j , k_m^j , for $j = 1, \dots, r$, so that the functions $m_{i(s)}$, $m_{i(Ac)}$, $m_{i(Me)}$, as defined by the equations (9) – (12), at the points $0 < t_1 < t_2 < \dots < t_r = T$ took on the values acquired experimentally in their measurements.

The function k_h can be determined using the method of selecting the best estimator in each range (t_{j-1}, t_j) . This problem has been solved by bringing it to the problem of filtration, characterized as follows.

The assumption was made that the waste distribution in the landfill, depending on variable environmental factors, may be described by the stochastic process $(Z_t)_{t \geq 0}$, being dependent on the unknown process $(X_t)_{t \geq 0}$. The stochastic process $(Z_t)_{t \geq 0}$ is described by the equation [16]:

$$dZ_t = G(t)X_t dt + D(t)dV_t,$$

while the unknown process $(X_t)_{t \geq 0}$, by the equation:

$$dX_t = F(t)X_t dt + C(t)dU_t,$$

where: $(U_t)_{t \geq 0}$ and $(V_t)_{t \geq 0}$ are stochastically independent Brown motions within the space (Ω, F, P) .

The solution of the filtration problem involves determining, based on the observation of the process $(Z_t)_{t \geq 0}$, another process $(\hat{X}_t)_{t \geq 0}$ which is the best estimator of process $(X_t)_{t \geq 0}$ influencing the course of the process $(Z_t)_{t \geq 0}$ being observed. To determine the estimator $(\hat{X}_t)_{t \geq 0}$, the Kolman-Bucky theorem should be applied.

According to the theorem, the process $\left(\hat{X}_t \right)_{t \geq 0}$ defining the best estimators of random variables X_t for $t \geq 0$, determined on the basis of the observation process $(Z_t)_{t \geq 0}$, satisfies the equation:

$$\begin{cases} d\hat{X}_t = \left(F(t) - \frac{G^2(t)S(t)}{D^2(t)} \right) \hat{X}_t dt + \frac{G(t)S(t)}{D^2(t)} dZ_t, \\ \hat{X}_o = EX_o \end{cases}$$

where, $S(t) = E(X_t - \hat{X}_t)^2$ satisfies the Riccati equation:

$$\begin{cases} dS(t) = 2F(t)S(t) - \frac{G^2(t)}{D^2(t)} S^2(t) + C^2(t) \\ S_{(o)} = E(X_o - EX_o)^2 \end{cases}$$

RESULTS

Waste characteristics

The chemical properties and composition of MSW and PMSW are presented in Table 1 below.

Table 1. Chemical properties and composition of the wastes (average of 10 samples)

Waste properties	MSW	PMSW
Moisture content, %	38.5±4.0	32.7±2.6
Volatile solid, % of dry matter	54.0±3.1	44.2±3.3
Organic carbon, kg/kg of dry matter	0.40±0.03	0.31±0.02
Biodegradable carbon, kg/kg dry matter	0.112±0.022	0.047±0.008
Biogas overall production, dm ³ /Mg	145±18.4	50±6.2
Total nitrogen, kg/kg dry matter	0.012±0.002	0.014±0.002
Composition of the waste (average percentage wet weight)		
Food and vegetable leftovers	43.6±7.1	32.4±7.4
Paper and cardboard	18.9±3.7	15.2±2.5
Glass	9.3±4.7	12.9±2.1
Plastic	13.0±2.6	18.3±5.7
Textile	2.3±1.5	2.7±1.4
Packing material (miscellaneous composition)	2.5±0.9	3.5±0.8
Wood	0.1±0.2	0.1±0.1
Metal	1.5±1.2	2.0±1.1
Mineral waste	8.8±3.3	12.9±4.6
Overall	100	100

Experimental results

Figure 2 presents the total biogas production expressed as grams of organic carbon mass that had been removed with biogas to one kilogram of MSW and PMSW waste. Figure 3

presents methane concentration in biogas. After the analysis of biogas production and methane concentration, three periods have been distinguished:

- First period – between the 1st and 105th day in the MSW bunker, and 91st day in the PMSW bunker. Characterized by quick gas production, there was no presence of methane detected. The total biogas production during this period reached 0.27 gC/kg in the MSW bunker and 0.12 gC/kg in the PMSW bunker;
- Second period – between the 106th and 448th day in the MSW bunker (92nd – 503rd in the PMSW bunker), characterized by the fast increase of methane level in biogas: up to 54% in the MSW and 65% in the PMSW bunker. Slightly slower than during the previous period was the daily production of biogas. On the last day of the second period a total biogas production in the MSW and the PMSW bunkers reached 0.89 gC/kg and 0.46 gC/kg respectively;
- Third period – from the 449th day (MSW) and the 504th day in the PMSW until the end of the research. The characteristic feature of this period was the slow decline in daily biogas production in the MSW bunker (the total biogas production on the last day of research reached 1.26 gC/kg), and a very low daily biogas production in the PMSW bunker (the total biogas production on the last day of research was 0.57 gC/kg). During this period, the concentration of methane maintained relatively a constant high level (an average methane concentration in biogas was approximately 55% in the MSW bunker and 66% in the PMSW bunker).

Figure 4 represents sum curves of TOC loads, removed with leachate from the MSW and PMSW. Within the first two months 0.14 gTOC/kg of waste was removed from the MSW bunker, which constituted 24% of the load emitted during the whole research. The TOC load removed from the PMSW bunker was approximately six times lower than the load removed from the MSW bunker.

During the following months of research, changes of curves representing TOC emissions in the MSW and PMSW bunkers were very similar. The overall TOC load

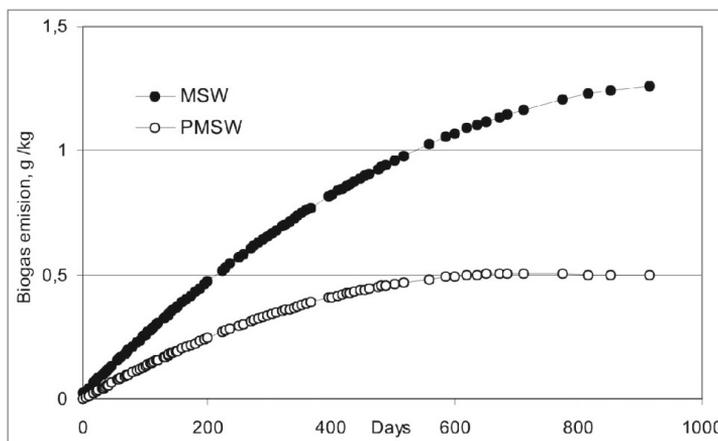


Fig. 2. The total curve of organic carbon emission in biogas from the MSW and the PMSW bunkers

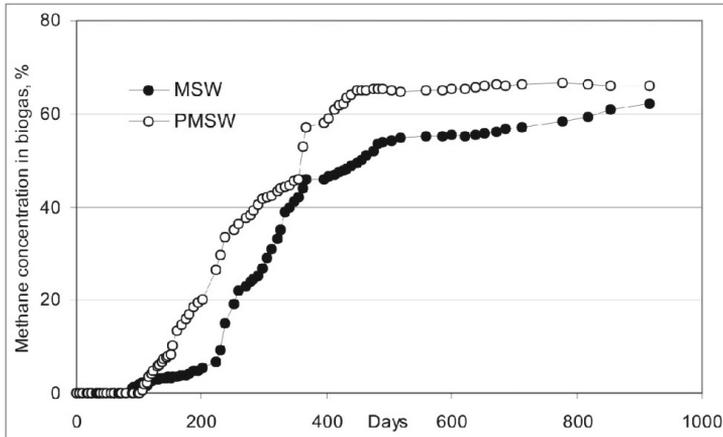


Fig. 3. The methane concentration in biogas from the MSW and the PMSW bunkers

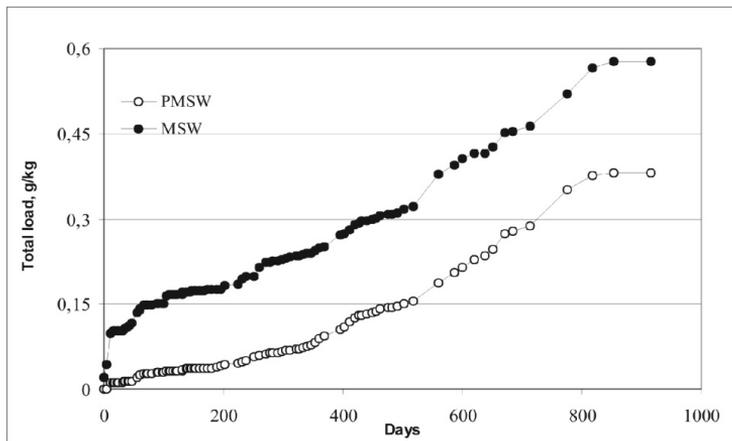


Fig. 4. TOC load removed in leachate from MSW and PMSW

removed from the MSW and PMSW bunkers, within 915 days of research, reached 0.58 and 0.38 gTOC/kg respectively.

Modeling results

The average values of decomposition rate constants during each phase (hydrolysis – k_h ; acid – k_a and methane – k_m) prior to and after biological processing – as presented in Table 2 – were determined upon the research results in scope of organic carbon emission from the MSW and PMSW in leachate (Fig. 4) and biogas production (Fig. 2), as well as the methane concentration in biogas (Fig. 3). To assess these values, modified equations of Zacharof and Butler's model were employed.

Table 2. The rate constants for hydrolysis, acid phase and methane phase of MSW and PMSW

Rate constants, d ⁻¹	Bunkers	
	MSW	PMSW
kh	2.6×10 ⁻⁵	3.3×10 ⁻⁵
ka	4.1×10 ⁻⁴	4.6×10 ⁻⁴
km	2.2×10 ⁻⁴	2.7×10 ⁻⁴

DISCUSSION

Experimental results

After 915 days of research, the total emissions of organic carbon removed from MSW and PMSW in biogas reached 1.26 g/kg, and PMSW 0.57 g/kg respectively. In the case of PMSW, the lower biogas production was the consequence of their preliminary oxygen stabilization prior to its deposit [2, 19, 21], which removed most of the organic, rapidly biodegradable substances from the waste. Biogas from the PMSW bunker had a higher methane concentration, in comparison with biogas from the MSW bunker. The average methane concentration in each bunker during the third phase of the process was 66% for the PMSW bunker, and 55% for the MSW.

As expected, the total TOC load removed from unprocessed waste in leachate was 65% lower than from PMSW waste. This finding is confirmed by numerous publications and research, which indicate that the organic pollution loads removed in leachate from the waste, after they had been biologically stabilized, may be 80–90% lower than in the case of raw waste [2, 19, 22]. Another finding is that 5-week oxygen processing of the waste before it was deposited is not sufficient to make it stabilized.

Modeling results

The determined rate constants of hydrolysis, acid phase and methane phase of unprocessed MSW fit within a wide range of values, as presented in the literature [7–10, 12, 13, 15, 25], and their proportions had similar tendencies in terms of changes (the hydrolysis constant had the lowest value, the acid phase constant was the highest) (Table 2).

The PMSW decomposition rate constants displayed similar change tendencies to those observed in the MSW during corresponding phases. However, their values were higher: $k_h - 21$, $k_a - 11$ and $k_m - 19\%$.

The higher values for PMSW may be explained by:

- Higher shredding of the PMSW, hence making the bigger area of waste available for microorganisms (during the aerobic stabilization the waste was moved five times);
- Higher susceptibility to anaerobic biodegradation of waste, previously processed aerobically, as indicated in research of Capella *et al.* [3].

The hydrolysis rate constant fit into ranges usually presented in the literature. According to Garcia de Cortazar and Monzon [7] the value of hydrolysis constant for readily biodegradable MSW fraction is $2.3 \cdot 10^{-4} \text{ d}^{-1}$, and for slowly biodegradable fraction – 10^{-7} d^{-1} . Likewise, Manna *et al.* [13] determined the first order hydrolysis constant for organic waste at $1.89 \cdot 10^{-3} \text{ d}^{-1}$.

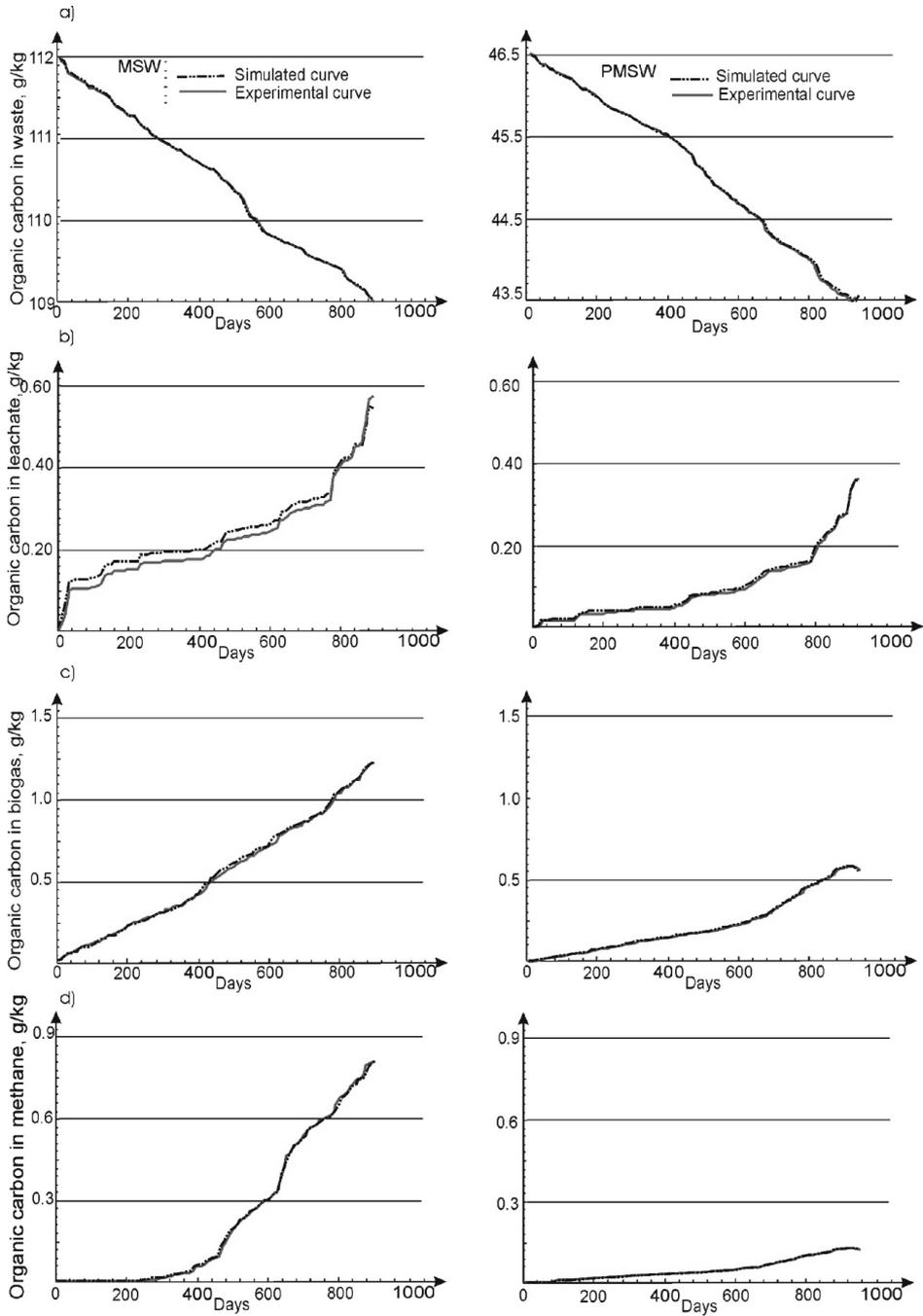


Fig. 5. Simulated and experimental curves determined for the MSW and PMSW waste, stored in conditions of technical: a) organic carbon mass loss, b) dissolved carbon mass, emitted in leachate, c) carbon mass emitted in biogas, d) carbon mass emitted in methane (methane phase)

On the other hand, the hydrolysis constant for PMSW, outlined in the research was visibly lower than the values presented in the literature. The constant value of first order hydrolysis for paper waste, agricultural waste and food leftovers, determined by Komilis *et al.* [10], was 0.005; 0.008 and 0.05 d⁻¹ respectively. Musmeci [15] found the value of hydrolysis rate constant for composted waste (consisting of grass, leaves and cardboard, in different proportions) between 0.165 and 0.190 d⁻¹.

Major divergences between hydrolysis constant values presented by different authors prove to what extent the chemical compositions of the waste and its landfill conditions influence the degradation rate. The quoted research regarding the PMSW degradation rate was conducted in laboratory conditions, with controlled temperature and waste moisture content. On the other hand, the research presented here, which allowed for establishing the constant values, was conducted in real conditions. Hence, the changeable weather conditions (temperature, rainfall) and, more importantly, uneven irrigation (being the consequence of heterogeneous nature of the landfill) had a considerable influence on the rate of processes taking place in landfills. Figure 5 presents experimental and simulated curves of carbon mass changes in PMSW and MSW, as well as in removed leachate and biogas. The curves run is based upon determined degradation rate constants k_h , k_a , k_m .

As a result, it was found that the experimental and simulated curves have accurate fit, both in the case of MSW and PMSW (Fig. 5). Coefficient of determination R² characterized the fit of the experimental curves to simulated [23] determined for waste processed and unprocessed in aerobic condition had very high values in the range 0.9–1. This proves that the equations (9–12) utilized to simulate degradation processes precisely reflect degradation processes both for biologically unprocessed and processed waste.

Changes the mass of carbon in the aerobically treated and untreated waste determined based on the unmodified equation Zacharof'a and Butler'a [30] (equations 4–7) characterized the low accuracy of the mapping (R² ratio of 0.5–0.6).

Obtaining a good level of fitting of the simulated curves to the experimental curves requires, however, many years' monitoring of the amount of leachate formed, biogas output quantity, organic carbon concentration in leachate, methane concentration in the biogas taken up, as well as the biodegradable carbon content and gas potential of the waste. In practice, the proposed model may be applied for prognosis of variations the mass of biodegradable carbon in waste, leachate and biogas.

The reliability of the prognosis depends on the duration of monitoring. In the case when conducting monitoring in real conditions is not feasible, there is a possibility of applying testing results derived from landfills with similar climatic conditions, provided that the initial organic carbon content and methane potential of the waste are known. Variations in the masses and concentrations of nitrogen, phosphorus and other contaminants in the leachate may be also prognosis on the basis of the model.

CONCLUSIONS

Based upon the results of presented research, the following conclusions may be drawn:

1. The five-week aerobic MSW stabilization before landfill, conducted in chambers with regular shoveling, reduces the TOC emission by 55% in biogas, and by 65% in leachate, when compared to unprocessed waste emission.

2. The anaerobic degradation processes in the municipal waste landfill are faster than in unprocessed MSW landfill, when such waste had been previously subjected to aerobic biological stabilization. Further research is required to verify and explain the observed processes.
3. The research confirmed that models employing the equation of first order reaction kinetics to evaluate the hydrolysis processes, as well as stochastic equations utilized to simulate the run of acid and methane phases are appropriate to describe the course of decomposition processes with regards to the MSW and PMSW landfills.

REFERENCES

- [1] Bastone, D.J., Keller, K., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., Vavilin, V.A. (2002). *Anaerobic digestion model no 1*, Scientific and Technical Report, **45**, 65–73.
- [2] Brinkmann, U., Höring, K., Heim, M., Ehrig, H.J. (1995). *Effect of pre-composting on the long-term behaviour of MSW landfills*. In Christensen, T.H., Cossu, R. & Stegmann, R. (Eds.), *Proceedings Sardinia '95*, Fifth International Landfill Symposium (pp. 971–985). Sardinia 1995.
- [3] Capella, I.F., Azeiteiro, C., Arroja, L., Duarte, A.C. (1999). *Effects of pre-treatment (composting) on the anaerobic digestion of primary sludges from a bleached kraft pulp mill*. In Mata-Alvarez, J., Tilche, A., Cecchi, F., (Eds.), *Proceedings of the International symposium on anaerobic digestion of solid waste* (pp. 113–120). Barcelona 1999.
- [4] Council Directive 1999/31/EC as of 26 April 1999 on waste landfill, subsequently amended by the Regulation of the European Parliament of the 1st Council (EC), no 1882/2003 (EC Official Journal L 182 as of 16th of July 1999, page 1 with subsequent amendments).
- [5] El-Fadel, M., Fidikakis, A.N., Leckie, J.O. (1996). *Numerical modeling of generation and transport of gas and heat in sanitary landfills: II. Model Formulation*, *Waste Management & Research*, **14**, 537–551.
- [6] El-Fadel, M., Fidikakis, A.N., Leckie, J.O. (1997). *Numerical modeling of generation and transport of gas and heat in sanitary landfills: III. Sensitivity analysis*, *Waste Management & Research*, **15**, 537–551.
- [7] Garcia de Cortazar, A.L., Monzon, T.I. (2007). *Application of simulation models to the diagnosis of MSW landfills: an example*, *Waste Management*, **27**, 691–703.
- [8] Haarstrick, A., Hempel, D.C., Ostermann, L. Ahrens, H., Dinkler, D. (2001). *Modeling of the biodegradation of organic matter in municipal landfills*, *Waste Management & Research*, **19**, 320–331.
- [9] Jokela, J.P., Vavilin, V.A., Rintala, J.A. (2005). *Hydrolysis rate, methane production and nitrogen solubilisation of grey waste components during anaerobic degradation*, *Bioresource Technology*, **96**, 501–508.
- [10] Komilis, D.P., Ham, R.K., Stegmann, R. (2006). *The effect of landfill design and operation practices on waste degradation behavior: a review*, *Waste Management & Research*, **17**, 20–26.
- [11] Lebiocka M., Montusiewicz A., Pawłowska M., Ozonek J., Szkutnik E., Roslan M. (2008). *Influence of ozonation on leachate quality from landfills with different degrees of solid waste pre-treatment*, *Archives of Environmental Protection*, **34**, 63–70.
- [12] Lee, J.J., Jung, I.H., Lee, W.B., Kim, J.O. (1993). *Computer and experimental simulations of the productions of methane gas from municipal solid waste*, *Water Science and Technology*, **27**, 225–234.
- [13] Manna L., Zannetti M.C., Genon G. (1999). *Modeling biogas production at landfill site*, *Resources Conservation and Recycling*, **26**, 1–14.
- [14] McBean, E., Rovers, F., and Farquhar, G. (1998). *Solid Waste Landfill Engineering and Design*, Prentice-Hall Publishing Co. Inc., Englewood Cliffs, New Jersey 1995.
- [15] Musmeci, L. (1998). *Organic fraction of municipal solid waste (OFMSW): extent of biodegradation*, *Waste Management*, **16**, 103–107.
- [16] Oksendal, B. (2000). *Stochastic differential Equations*, Springer, Berlin, 2000.
- [17] Pohland, F.G., Ghosh, S. (1971). *Developments in anaerobic stabilization of organic wastes-the two phase concept*, *Environmental Letters*, **1**, 255–266.
- [18] Reinhart, D.R., Al-Yousfi A.B. (1996). *The impact of leachate recirculation on municipal solid waste landfill operating characteristics*, *Waste Management & Research*, **14**, 337–46.

- [19] Robinson, H.D., Knox, K., Bone, B.D. (2004). *Improved definition of leachate source term from landfills Phase 1: review of data from European landfills*, Science Report Environment Agency 2004.
- [20] Sanphoti, N., Towprayoon, S., Chaiprasert, P., Nopharatana, A. (2006). *The effects of leachate recirculation with supplemental water addition on methane production and waste decomposition in a simulated landfill*, Journal of Environmental Management, **81**, 27–35.
- [21] Schön, M.: *Verfahren zur Vergärung organischer Rückstände in der Abfallwirtschaft*, Verlag E. Schmidt GmbH & Co., Berlin 1994.
- [22] Stegman, R. (1991). *Vorteile der Restmüll – Aufbereitung zur Senkung der Gasemissionen von Deponien. Aufbereitung fester Siedlungsabfälle vor der Deponierung*, Zentrum für Abfallforschung, Technical University of Braunschweig, **6**, 341–359.
- [23] Vanrolleghem, P.A., Insel, G., Peterson, B., Sin, G., De Pauw, D., Nopens, I., Dovermann, H., Weijers, S., Gernaey, K. (2003). *Comprehensive model calibration procedure for activated sludge model*. In Proceedings 76th Annual Technical Exhibition and Conference. October 11–15, Los Angeles, CA, USA 2003.
- [24] Vavilin, V.A., Rytov, S.V., Lokshina, L.Y. (1996). *A description of hydrolysis kinetics in anaerobic degradation of particulate organic matter*, Bioresource Technology, **56**, 229–237.
- [25] Vavilin, V.A., Lokshina, L., Jokela, J.P.Y., Rintala, J.A. (2004). *Modeling solid waste decomposition*, Bioresource Technology, **94**, 69–81.
- [26] Vavilin, V.A., Fernandez, B., Palatsi, J., Flotats X. (2008). *Hydrolysis kinetics anaerobic degradation of particulate organic material: An overview*, Waste Management, **28**, 939–951.
- [27] Waste Management Act, as of 27 April 2001 (Journal of Laws, 2001.62.628).
- [28] Young, A. (1989). *Mathematical modeling of landfill degradation*, Journal of Chemical Technology & Biotechnology, **46**, 189–208.
- [29] Young, A. (1995) *Mathematical modeling of the methanogenic ecosystem*, Microbiology of landfill sites, Lewis Publisher, USA.
- [30] Zacharof, A.I., Butler, A.P. (2004) *Stochastic modeling of landfill processes incorporating waste heterogeneity and data uncertainty*, Waste Management, **24**, 241–250.

STAŁE KINETYCZNE ROZKŁADU ZMIESZANYCH ODPADÓW KOMUNALNYCH PRZED I PO MECHANICZNO-BIOLOGICZNYM PRZETWORZENIU. SKALA POŁOWA

Istotnym zadaniem gospodarki odpadami komunalnymi w krajach UE jest systematyczne zmniejszanie ilości odpadów komunalnych usuwanych na składowiska, w tym zwłaszcza odpadów ulegających biodegradacji. Jedną z metod stosowanych do realizacji tego celu jest mechaniczno-biologiczne przetwarzanie odpadów komunalnych (MBP) przed ich składowaniem. W artykule przedstawiono charakterystykę surowych odpadów komunalnych (ZOK) i wstępnie przetworzonych biologicznie, ładunki węgla organicznego emitowane w biogazie i odciekach podczas ich składowania oraz wyznaczono stałe szybkości rozkładu tych odpadów w oparciu o zmodyfikowany stochastyczny model Zacharof'a i Butler'a. Wartości wyznaczonych dla ZOK stałych szybkości rozkładu mieściły się w bardzo szerokich zakresach prezentowanych w literaturze, a ich relacje zachowywały podobne tendencje zmian; stała hydrolizy miała najniższą wartość ($2,6 \times 10^{-5} \text{ d}^{-1}$), co potwierdziło limitujący jej wpływ na szybkość rozkładu, stała fazy kwaśnej najwyższą ($4,1 \times 10^{-4} \text{ d}^{-1}$), a stała fazy metanowej – $2,2 \times 10^{-4} \text{ d}^{-1}$). Stałe szybkości rozkładu PMSW w poszczególnych fazach beztlenowej degradacji odpadów zachowywały podobne tendencje zmian, jednakże ich wartości były wyższe, odpowiednio o 21, 11 i 19%.